

# EXHIBIT X



# Oxidation induced embrittlement in polypropylene — a tensile testing study

B. Fayolle, L. Audouin \*, J. Verdu

*ENSAM, 151 Boulevard de l'Hopital, 75013 Paris, France*

Received 14 June 2000; accepted 27 June 2000

## Abstract

The thermal oxidation of polypropylene films (100  $\mu\text{m}$ ) in air at 90°C was studied by IR spectroscopy, rheometry at 210°C and tensile testing. Tensile testing reveals a sudden embrittlement before the end of the induction period determined from carbonyl build up curves. Embrittlement occurs at a very low conversion of the chain scission process (only 1 chain scission per 3 initial chains) and it can be demonstrated that it results from a decrease in polymer toughness rather than from the build up of defects linked to a presumed heterogeneity of the oxidation process. Tensile testing is not necessarily a good tool to characterize embrittlement given that phenomena such as necking and crack initiation at geometric defects are not taken into account with the usual measuring methods. The sudden drop of ultimate elongation could be, at least partly, an artifact. © 2000 Published by Elsevier Science Ltd. All rights reserved.

**Keywords:** Polypropylene; Oxidation; Embrittlement; Lifetime; Chain scission

## 1. Introduction

Tensile testing is widely used to monitor the ageing of initially ductile polymers such as polyolefins [1,2]. A change of tensile properties can result from two main causes: (i) “annealing” effects linked to the fact that the polymer is initially out of equilibrium: post crystallization, orientation relaxation, etc. These effects occur generally shortly after the beginning of exposure and can affect the small strain properties (modulus, yield point). (ii) Ageing effects are essentially linked to modifications of the macromolecular skeleton (crosslinking, chain scission). These effects are generally responsible for long term embrittlement, and they practically do not affect the small strain properties.

This article deals with the ageing effects associated with the thermal oxidation of polypropylene films and we try to answer the following questions: is it possible to establish a link between the change of tensile properties and the structural changes in the polymer, in particular the amount of chain scission or the conversion of the

oxidation process? Is it appropriate to use tensile properties as chemical variables in kinetic modelling? Is tensile testing the most pertinent mechanical testing method?

Indeed, two cases are to be distinguished: thin samples in which ageing is not controlled by the diffusion of oxygen, so that degradation is homogeneous and embrittlement results directly from structural changes, and bulk samples in which ageing takes place mainly at a superficial layer, so that damage may result from density gradients. The present work is devoted to the first case, i.e. to the “intrinsic” effect of ageing in polymer embrittlement.

A relatively well known case, i.e. polypropylene thermal oxidation, has been chosen. The advantage of PP is that it oxidises relatively fast in solid state and it predominantly undergoes chain scission.

## 2. Experimental

Experiments were made on  $100 \pm 2 \mu\text{m}$  extruded films of stabilised isotactic polypropylene supplied by Atochem. Steric exclusion chromatographic (SEC) measurements after extrusion gave average molar mass values of  $M_n = 55 \text{ kg mol}^{-1}$  and  $M_w = 266 \text{ kg mol}^{-1}$ . The additives

\* Corresponding author. Tel.: +33 1 4424 6413; fax: +33 1 4424 6382.

E-mail address: ltvp@paris.ensam.fr (L. Audouin).

were extracted for 30 h in a Soxhlet extractor using a ternary solvent mixture (hexane/chloroform/ethanol 4:1:1) [3]. The films were then dried for 48 h at 40°C under vacuum. Thermal ageing was studied in air at 90°C using a ventilated oven regulated at  $\pm 1^\circ\text{C}$ .

Dogbone samples were cut with a MTS H2 stamp after ageing. They had a calibrated length of 25 mm and a width of 4 mm. A good quality of cutting is necessary to avoid the presence of defects capable of initiating cracks.

Tensile tests were performed on an Instron 4502 dynamometer with a strain rate of  $50\text{ mm min}^{-1}$  ( $33 \times 10^{-3}\text{ s}^{-1}$ ) using a measurement cell of 1 kN full range with a relative error of 0.5%. Only engineering stresses and strains will be reported here; no corrections will be made for thickness and width changes.

IR spectroscopic measurements were made on a Bruker IFS 28 spectrophotometer with a resolution of  $4\text{ cm}^{-1}$ .

The zero shear viscosity  $\eta_0$  was obtained in dynamic oscillatory mode with a Rheometrics Scientific ARES rheometer using parallel plate geometry (plate diameter 25 mm and gap 0.5 mm). The tests were performed under nitrogen at 210°C with frequencies ranging between 0.05 and 512  $\text{rad s}^{-1}$  and with a maximum strain amplitude optimised to measure reliable torque values (in the linear viscoelastic domain). In order to avoid secondary thermolysis in the rheometer cell, the films were previously treated with sulfur dioxide to destroy hydroperoxides. After a 24 h treatment at ambient temperature, no subsequent thermal degradation was observed during rheometric measurements. Molar mass was determined at 210°C according to:  $\eta_0 = K.M_w^{3.4}$  where  $\eta_0$  is in Pa s and  $M$  in  $\text{g mol}^{-1}$ . The constant  $K$  value of  $1.072 \times 10^{-15}$  was determined by SEC and viscosity measurements performed on the virgin polymer.

### 3. Results

#### 3.1. Yield stress

Yield stress ( $\sigma_y$ ) remains constant as long as it can be observed. After 150 h of exposure embrittlement occurs: the yield vanishes and brittle fracture takes place (see Fig. 1; ductile–brittle transition is indicated by dashed line). It can be thus concluded, that the yield stress is not very sensitive to structural changes in the polymer induced by the oxidation process. This is not surprising since it is well known that, in polyolefins, the yield stress depends essentially on the crystallinity ratio, especially through the crystallite thickness [4]. If the oxidation takes place only in the amorphous phase, it is expected to have little or no influence on the yield properties except when extensive chain scissions result in chemicrystallisation [5]. In this case, some increase of yield stress could be

expected but in our case such phenomenon was undetectable. It can be concluded that yield properties are not a convenient means of evaluating polymer ageing.

#### 3.2. Ultimate elongation

The change of ultimate elongation ( $\epsilon_R$ ) during ageing is presented in Fig. 2. The ultimate elongation ( $\epsilon_R$ ) remains almost constant at 800% during the initial period of exposure and decreases abruptly after  $150 \pm 30$  h to reach a value close to the initial yield strain of 13%. An induction time may thus be defined as the time elapsed from the beginning of exposure to this ductile–brittle transition. The kinetic curve of carbonyl build-up has been also included in Fig. 2. It displays an induction time  $t_{iCO} = 250 \pm 10$  h determined by intersection between tangent at inflexion point and time axis. These results call for the following comments.

- Embrittlement is a catastrophic process that can be described as a relatively sharp transition between a ductile and a brittle state.
- For the polymer under study embrittlement occurs at a very low conversion of the oxidation, as seen from the fact that the induction time,  $t_{iCO}$ , determined from spectrophotometric measurements is significantly longer than the induction time determined from the variations of ultimate strain with time, i.e. less than 150 h against 250 h for  $t_{iCO}$ . Although this fact has been already reported [6] it has never been, to our knowledge, quantitatively studied. After 250 h exposure at 90°C, the concentration of carbonyl groups (the main oxidation products) is less than  $5 \times 10^{-3}\text{ mol kg}^{-1}$ . Since the monomer unit concentration is about  $24\text{ mol kg}^{-1}$ , we can reasonably estimate that at the moment of brittle failure the conversion of the oxidation reaction is lower than  $5 \times 10^{-4}$  (0.05%). It is worth mentioning that the initial chain concentration is  $M_{n0}^{-1} = 0.018\text{ mol kg}^{-1}$ . Thus, even if the chain scission yield would have been very high (i.e. one chain scission per carbonyl group), we would have still had less than one chain scission per initial polymer chain at the embrittlement point.

#### 3.3. Ultimate stress

The failure envelope: ultimate stress ( $\sigma_R$ ) against ultimate strain ( $\epsilon_R$ ) for every individual tests is presented in Fig. 3. As previously found for many polymers in the case of photo-oxidation [7], this curve corresponds to the virgin polymer tensile curve, a fact that calls for the following comments:

- Changes of sample cross-section are not taken into account in the usual procedure thus the failure

envelope can not be considered as an intrinsic property of the material.

- (ii) The stress values, even after correction for cross-section area, are representative of the average stress state on the whole sample volume whereas rupture is a local phenomenon initiated at pre-existing defects on the edges of the sample. These defects concentrate stresses so that the true stress responsible for rupture is always higher than the measured “average” stress.

- (iii) As evidenced in Figs. 2 and 3, the ultimate elongation ( $\epsilon_R$ ) varies monotonically with ageing time and displays an abrupt change indicative of a ductile–brittle transition. So it can be thus used as an ageing function whereas the ultimate stress ( $\sigma_R$ ) varies non-monotonically with ageing time, increasing after embrittlement (Figs. 1 and 3). This latter depends of the shape of the tensile curve  $\sigma = f(\epsilon)$ . It could be schematically written:

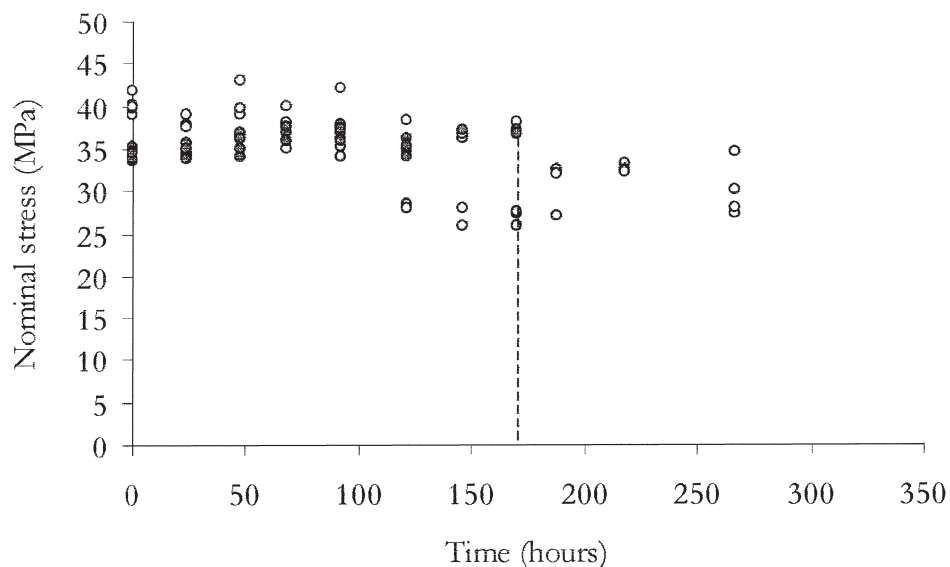


Fig. 1. Evolution of yield stress (L) and ultimate stress (O) during exposure, ductile–brittle transition is indicated by dashed line.

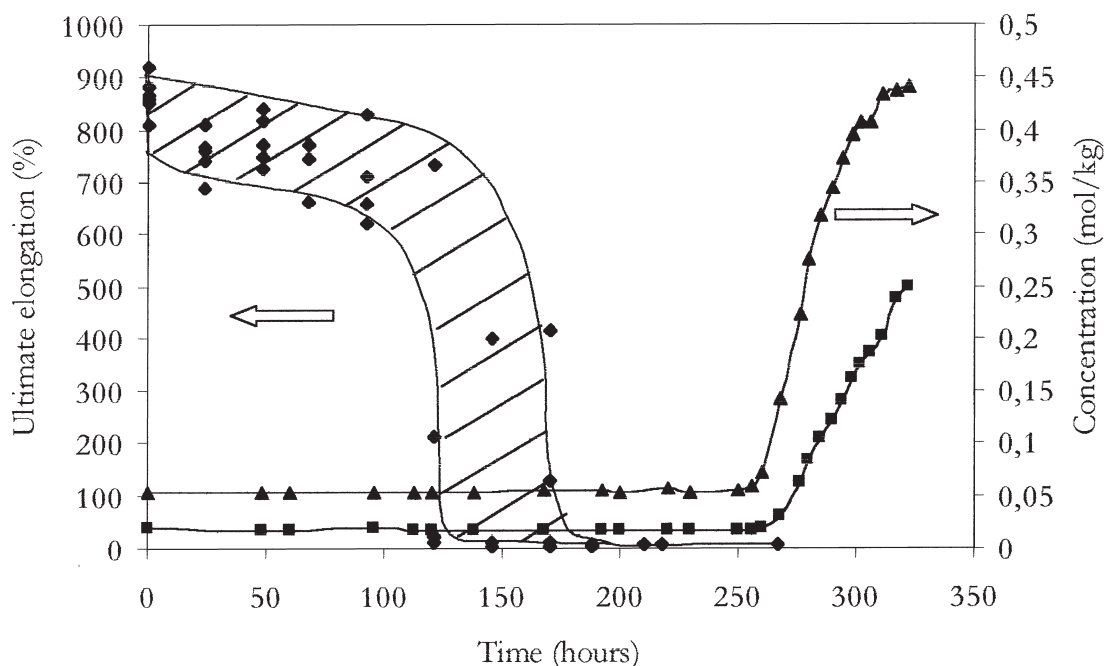


Fig. 2. Evolution of ultimate elongation (◆) during exposure and kinetic curves of carbonyl at  $1710\text{ cm}^{-1}$  (■) and of OH groups at  $3410\text{ cm}^{-1}$  (▲) build up.

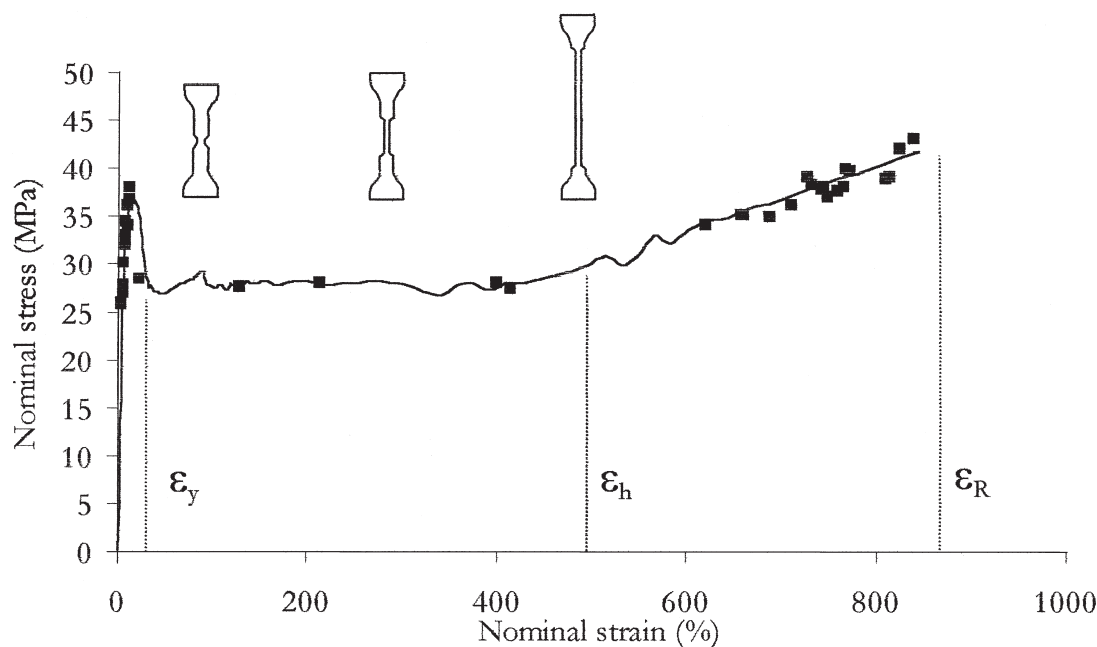


Fig. 3. Failure envelope ( $\sigma_R$  vs  $\varepsilon_R$  during exposure) (■) and tensile curve of unaged specimen in nominal strain–stress coordinates (—).

$$\frac{d\sigma_R}{dt} = \frac{d\sigma_R}{d\varepsilon_R} \frac{d\varepsilon_R}{dt}$$

where  $\frac{d\varepsilon_R}{dt}$  depends essentially on ageing time and is always negative whereas  $\frac{d\sigma_R}{d\varepsilon_R}$  depends on mechanical behaviour of the sample and can be positive or negative depending on the predominating deformation process (plastic instability at the yield point, orientation hardening, etc.). These observations are valid in the case of thermal oxidation [8] as well as in the case of photo-oxidation [7].

#### 3.4. Viscosity measurements

The effect of ageing time on the viscosity curves of the oxidized polymer is illustrated in Fig. 4. The observed decrease in the Newtonian viscosity of the polymer as well as an extension of the Newtonian region clearly indicate a narrowing of the molecular weight distribution with ageing time [9]. The change of weight average molar mass  $M_w$  (calculated with scaling law at 210°C:  $\eta_0 = 1.072 \times 10^{-15} M^{3.4}$  after an ageing time of 100 h indicates that the chain scission process begins far before the end of the classical induction period  $t_{iCO}$  of 250 h (Fig. 5).

#### 4. Discussion

It is clear from the above results that as a consequence of ageing the PP oxidized samples reached a critical state where there is a sudden change from ductile to

brittle behaviour. From simple fracture mechanics considerations one can derive the following questions:

- Is tensile testing a pertinent tool to study embrittlement before PP oxidized is completely brittle, i.e.  $\varepsilon_R > \varepsilon_y$ ?
- Does the sudden change of ductile to brittle behaviour result from the existence of a critical structural state? The first structural variable which comes to mind is, indeed, the molar mass. Or does the change result from the existence of a critical defect size? This hypothesis would apparently agree with the theories according which oxidation is highly heterogeneous [10].

Let us now address the first question relative to the validity of tensile testing as a tool to study PP ageing before the ductile–brittle transition, i.e.  $\varepsilon_R > \varepsilon_y$ . To answer this question we need first to describe the mechanical behaviour of the polymer at large strains. A first problem comes obviously from the fact that the values of ultimate stress and elongation cannot be entirely considered as intrinsic material's property given that failure always occurs at a defect whose the nature and geometry are expected to play an important role in the fracture process. Let us recall the shape of the tensile curve in nominal strain–stress coordinates and the main steps of the deformation process (Fig. 3).

Between  $\varepsilon_y$  (yield strain) and  $\varepsilon_h$  (onset of the hardening process) necking propagates along the calibrated sample section. The draw ratio in the necking zone is constant so that the nominal strain at this stage of deformation is proportional to the size of plastic

instability. Thus, comparing the true strain  $\varepsilon_{tr}$  and the nominal strain  $\varepsilon_{nom}$ , it can be seen that they will be equal only when necking covers the whole calibrated length [11], i.e. when  $\varepsilon_{nom} = \varepsilon_h$ . Thus  $\varepsilon_h$  appears as the only strain value having a clear sense. It corresponds to the homogeneous draw ratio in the necking zone.

If failure occurs at a strain lower than  $\varepsilon_h$  (460% in our case, see Fig. 3), the corresponding strain value  $\varepsilon_R$  lacks

a physical meaning from the point of view of structure-property relationships, because fracture necessarily occurs at defects on the edges of the sample activated by the passage of the necking. Indeed, it is not possible to completely suppress such defects.

For strains higher than  $\varepsilon_h$  ( $\varepsilon_{nom} > 460\%$ ) hardening occurs in the calibrated part of the sample. This process is not homogeneous since there are hyper orientated

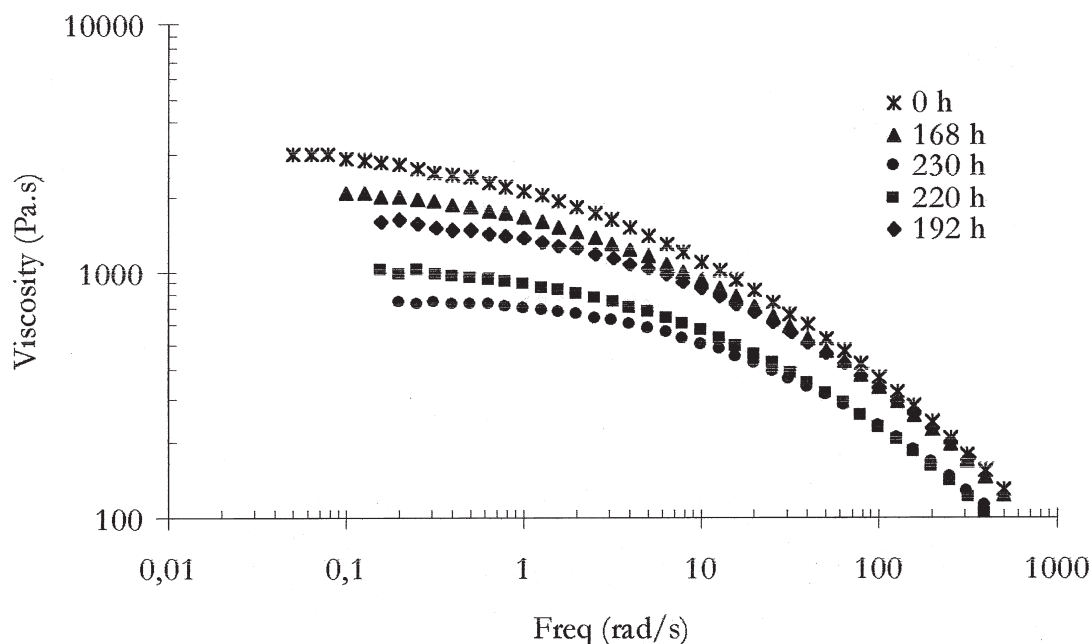


Fig. 4. Evolution of viscosity curves during exposure.

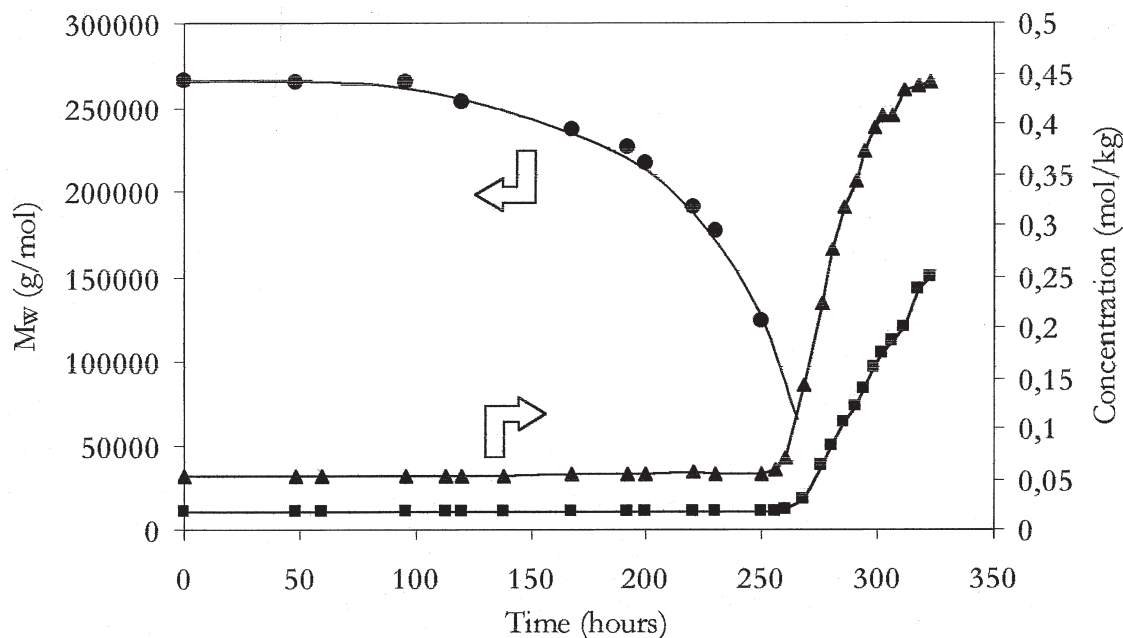


Fig. 5. Change of average molar mass weight  $M_w$  (●) during exposure and kinetic curves of carbonyl at  $1710\text{ cm}^{-1}$  (■) and of OH groups at  $3410\text{ cm}^{-1}$  (▲) build up.

domains which transmit loads to less orientated domains through a decrease of the cross sectional area. Fracture occurs when a hyper orientated domain contains a critical size defect. This is the reason why two tensile curves of the same material are almost identical except for the location of the rupture point (Fig. 3). At this stage of deformation, the behaviour is brittle, a defect creates a stress concentration and the material reaches locally its true ultimate stress. The fracture event would thus corresponds to the probability of an encounter between a hyper orientated domain and a defect on sample edges. This mechanism explains why the rupture points (coordinates  $\varepsilon_R$  and  $\sigma_R$ ) are always located on a master curve which is in fact the material's tensile curve. Thus neither  $\varepsilon_R$  nor  $\sigma_R$  may be considered as intrinsic material properties closely linked to the polymer structure. In fact, if we imagine an ageing process in which the true ultimate strain  $\varepsilon_{Rtr}$  would vary monotonically (Fig. 6a), we could expect a non monotonic variation of the nominal ultimate strain  $\varepsilon_{Rnom}$  as a result of the above described discontinuities (Fig. 6b).

It thus appears that the “transfer function” between the change of polymer structure due to the process of ageing and the change of its tensile properties (in nominal strain-stress coordinates) is relatively complex, tensile testing not being a pertinent experimental tool to study ageing of initially ductile polymers.

The answer to the second question seems quite straightforward in the case of amorphous polymers, or semi-crystalline polymers with low crystallinity ratio, for which it is well known [12,13] that the ductile-brittle transition corresponds to a critical structural state related to the entanglement threshold, the order of magnitude of the critical molar mass being generally  $M_C \approx 10 \text{ kg mol}^{-1}$ . It has been shown, for instance, that in the case

of polycarbonate hydrolysis embrittlement always occurs at  $M_C \approx 14 \text{ kg mol}^{-1}$  whatever the exposure conditions [14]; a value close to  $16 \text{ kg mol}^{-1}$  has been also found in the case of polyamide 11 [15].

The case of semi-crystalline polymers is somewhat more complicated owing to the important role of morphology. The toughness of virgin polymers represented by the critical rate of elastic energy release  $G_{IC}$ , increases with the molar mass but it does not display a catastrophic transition as in the amorphous polymers [12,16]. It is observed, for instance, that the crystallinity ratio of virgin polymers decreases when the chain length increases [16]. We can conclude that these virgin polymers with different chain length cannot be necessarily considered as good models of aged polymers of same molar mass.

This different behaviour can be attributed to differences in the molecular mechanisms of yielding: in amorphous polymers plastic deformation is directly linked to chain drawing through the entanglement network; in semi-crystalline polymers tie molecules interconnecting lamellae play a crucial role in process of yielding [17]. Thus in semi-crystalline polymers the critical structural variable could be the tie chain density (TCD) rather than the entanglement density (ED). The TCD depends of both morphology and molar mass [18,19] which in turn complicates the analysis.

There is an abundant literature on deformation mechanisms of semi-crystalline polymers [20] but the great diversity of cases makes difficult the drawing of a coherent synthesis. What seems clear, however, is that the tie chains present in the amorphous interlamellar zones play a key role in the plastic deformation by allowing load transfer between crystallites and the ensuing destruction of lamellar structure by chain slip and lamellar break-up [4]. The following causal chain may be thus proposed:

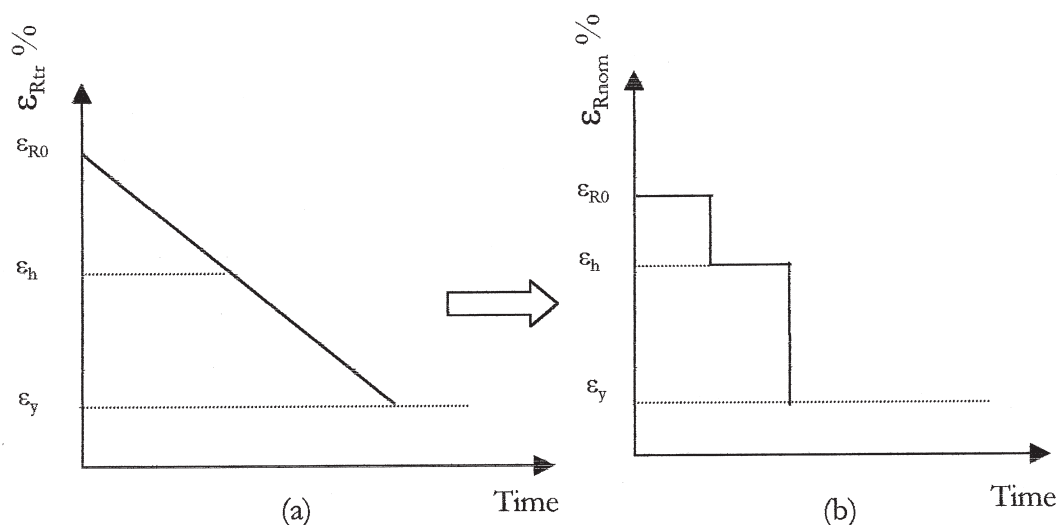


Fig. 6. (a) Hypothetical monotonic variation of the true ultimate strain  $\varepsilon_{Rtr}$ ; (b) expected non monotonic variation of nominal ultimate strain  $\varepsilon_{Rnom}$ .



Oxidation in the amorphous phase  $\Rightarrow$  chain scission  
 $\Rightarrow$  rupture of tie chains  
 $\Rightarrow$  loss of plasticity/ductility potential.

According to this causal chain and in order to predict ageing induced embrittlement we would need:

- (i) A kinetic model for oxidation.
- (ii) The identification of the chain scission mechanism and its yield in the corresponding elementary step of the mechanistic scheme.
- (iii) The structure of tie chains in order to determine/estimate the probability of chain scission on a tie chain (a part of chain scissions can occur in mechanically inactive chains).
- (iv) A criterion for the ductile–brittle transition, such as a critical fraction or concentration of residual tie chains.

Practically all these points remain at present time widely open research areas. Concerning the specific case of PP, an interesting characteristic which should orientate the discussion on points (iii) and (iv) above is the very high value of the “critical molar mass” for embrittlement: at the end of ductile–brittle transition ( $\sim 200$  h)  $M_{DB} \approx 200 \text{ kg mol}^{-1}$  (see Figs. 2 and 5), a value that is one or two orders of magnitude higher than the entanglement threshold [25] ( $M_C = 2M_E \approx 7 \text{ kg mol}^{-1}$ ). Two ways may in principle be envisaged for explaining this result.

(a) Oxidation is highly heterogeneous and creates mechanically active defects, i.e. oxidized domains having a size greater than a critical value and capable of initiating cracks at a stress close to the initial yield stress [10]. In this case the material’s toughness would remain almost constant, since there would be only very small structural (molar mass) changes in the whole polymer. There are, however, two strong arguments against this hypothesis: first SEC measurements do not allow us to observe the expected heterogeneity [21,22]. Second, let us also recall that virgin PP being relatively tough, its embrittlement would need the build-up of large visible defects. Such defects have never been observed in PP at low conversions of oxidation process (fortunately, relatively large scratches don’t lower significantly the impact resistance of PP bumpers for instance!).

(b) Embrittlement results from a homogeneous or pseudo-homogeneous polymer degradation process leading to a considerable decrease in toughness. The fact that embrittlement occurs at very low conversion could be then linked to some peculiar character of the tie chains. Let us for instance suppose that interlamellar ties consist of many entangled chains [23,24]. In this case, the critical molar mass for embrittlement ( $M_{DB}$ ) could be schematically expressed as a function of the molar mass between entanglements ( $M_E$ ), close to  $3.5 \text{ kg mol}^{-1}$  for PP [25]:

$$M_{DB} = b\lambda M_E$$

where  $b$  and  $\lambda$  are factors greater than one and related respectively to the number of entanglement strands in a given tie chain and to the critical fraction of ties chain allowing plastic deformation. A large value of the product  $b\lambda$ , on the order of 50, could then explain the high value of  $200 \text{ kg mol}^{-1}$  observed for  $M_{DB}$  in the case of PP. Can a critical molar mass of  $200 \text{ kg mol}^{-1}$  be generalized to all PP samples? Or is this value dependent on the initial PP structure (morphology, molar mass distribution)? Further research work is needed to answer these questions.

## 5. Conclusions

The thermo-oxidation of polypropylene films at  $90^\circ\text{C}$  has been studied by physico-chemical methods and by tensile testing. It displays the following main characteristics.

- (i) Ageing does not bring about significant changes in the low strain characteristics (yield point).
- (ii) The ultimate elongation drops suddenly from its initial value ( $\sim 800\%$ ) to the yield value (13%).
- (iii) Embrittlement occurs at very low conversion of the oxidation, when the molar mass is about  $200 \text{ kg mol}^{-1}$ , i.e. far above the entanglement critical molar mass.

Some practical and theoretical implications of these results have been discussed. It appears that classical methods for monitoring the process of ageing such as IR spectrophotometry and tensile testing in nominal strain–stress value are not necessarily the best tools to determine the polymer lifetime.

## References

- [1] Oswald J, Turi J. *Polym Eng Sci* 1965;5:152.
- [2] Wyzgoski MG. *J Appl Polym Sci* 1981;26:1689.
- [3] Zahradnickova A, Sedlar J, Dastych D. *Polym Degrad Stab* 1991;32:155.
- [4] Schultz JM. *Polym Eng Sci* 1984;24:770.
- [5] Mathur AB, Mathur GN. *Polymer* 1982;23:54.
- [6] Gensler R, Plummer CJG, Kausch HH, Kramer E, Pauquet JR, Zweifel H. *Polym Degrad Stab* 2000;67:195.
- [7] Pabiot J, Verdu J. *Polym Eng Sci* 1981;21:32.
- [8] Langlois V, Audouin L, Courtois P, Verdu J. *Angew Makromol Chem* 1993;208:47.
- [9] Bersted BH. *J Appl Polym Sci* 1975;19:2067.
- [10] Celina M, George GA, Billingham NC. *Polym Degrad Stab* 1993;42:335.
- [11] De Candia F, Romano R, Russo R, Vittoria V. *Colloid Polym Sci* 1987;265:696.
- [12] Greco R, Ragosta G. *Rubb Plast Process Applic* 1987;7:163.
- [13] Kausch H H. *Polymer fracture*. 2nd ed. Berlin/Heidelberg: Springer Verlag, 1987.



- [14] Gardner RJ, Martin JR. *J Appl Polym Sci* 1979;24:1269.
- [15] Driancourt A, Dalmaso F, Chaupart N. Modelization degradation mechanisms in aqueous environment of PA11 and criterion of lifetime. Colloque JSTMM 97, Durabilité des matériaux de structure, Nabeul, Tunisie, 3–4 November 1997.
- [16] Avella M, dell'Erba R, Martuscelli E, Ragosta G. *Polymer* 1993;34:2951.
- [17] Peterlin A. *J Mater Sci* 1971;6:490.
- [18] Keith HD, Padden Jr FJ, Vadimsky GJ. *Polym Sci A* 2 1966;4:267.
- [19] Ishikawa M, Ushui K, Kondo Y, Hatada K, Gima S. *Polymer* 1996;37:5375.
- [20] Lin L, Argon AS. *J Mater Sci* 1994;29:294.
- [21] Girois S, Audouin L, Verdu J, Delprat P, Marot G. *Polym Degrad Stab* 1996;51:125.
- [22] Achimsky L, Audouin L, Verdu J. *Polym Degrad Stab*, in press.
- [23] Flory PJ, Yoon DJ, Dill KA. *Macromolecules* 1984;17:862.
- [24] Plummer CJG, Kausch HH. *Macromol Chem Phys* 1996;197:2047.
- [25] Van Krevelen DW. *Properties of polymers*. 3rd ed. Amsterdam: Elsevier, 1990 p. 465.